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Supporting information**Broadband Dye-Sensitized Upconversion of Near-IR
Light**

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and Jan C. Hummelen^{1,2*}

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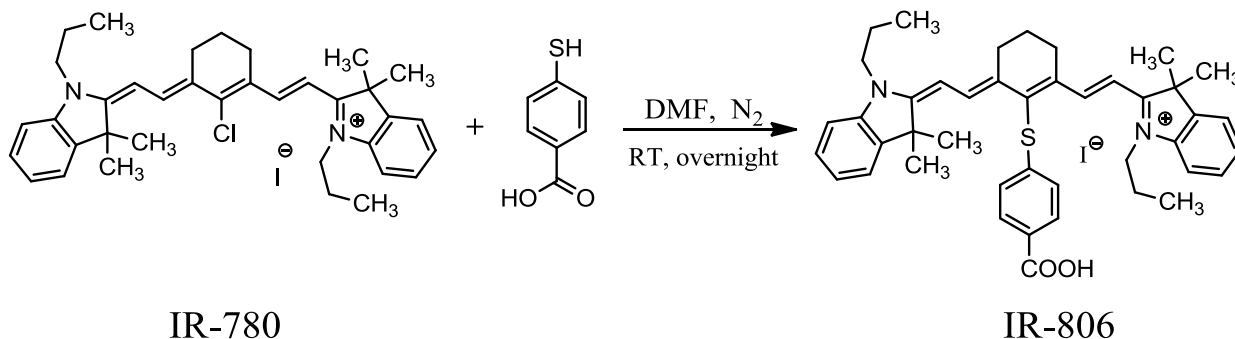
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A. Experimental part: general

General Chemicals. IR-780 iodide (99%), 4-mercaptobenzoic acid (99%), yttrium(III) oxide (Y_2O_3 , 99.99%), ytterbium (III) oxide (Yb_2O_3 , 99.9%), erbium (III) oxide (Er_2O_3 , 99.9%), trifluoroacetic acid (CF_3COOH , 99%), sodium trifluoroacetate (CF_3COONa , 98%), N,N -dimethylformamide (DMF, anhydrous, 99.8%), and chloroform (ACS spectrophotometric grade, $\geq 99.8\%$, with amylenes as stabilizer) were obtained from Aldrich. Oleylamine (C_{18} -content 80–90%) was purchased from Acros. Dichloromethane (DCM, AR grade) and diethyl ether (AR grade) were obtained from LAB-SCAN. Ethanol (absolute) was purchased from Merck. All chemicals were used as received. Lanthanide trifluoroacetate trihydrates ($\text{RE}(\text{CF}_3\text{COO})_3 \cdot 3\text{H}_2\text{O}$) were prepared by a method described in the literature.^[1]

Instrumentation. ^1H and ^{13}C NMR spectra were recorded on a Varian AMX400 (400 and 100.59 MHz, respectively) using CDCl_3 as solvent at room temperature. Spectra were referenced to the solvent line (CHCl_3 : 7.26 ppm for ^1H , 77.0 ppm for ^{13}C) relative to tetramethylsilane. Data are reported as follows: chemical shifts, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, t = triplet), coupling constants (Hz), and integration. FT-IR spectra were recorded on a Nicolet Nexus FT-IR spectrometer, using the SMART iTR for ATR measurements (diamond). Mass spectra were recorded on a LTQ Orbitrap XL (ESI+). Transmission electron microscopy (TEM) was performed on a Philips CM10 transmission electron microscope operating at an accelerating voltage of 100 kV. Images were recorded on a Gatan slow-scan CCD camera. UV-Vis absorption spectra were measured on a Perkin/Elmer Lambda 900 UV-Vis-NIR Spectrometer in chloroform in a quartz cuvette with a path length of 1 cm. Standard CW fluorescence measurements of solutions in chloroform were performed on a Fluorolog 3 (Jobin Yvon Horiba). For the up-conversion luminescence measurements, a Ti:Sapphire laser system (MIRA-900-F) was used as the excitation source. Luminescence spectra and lifetime measurements were performed in the cw and pulsed mode, respectively. In the latter case, the repetition rate was 76 MHz. The excitation light was focused into a 1 mm thick sample cell by a 75 mm focal length lens. This resulted in a focal spot of $120 \pm 10 \mu\text{m}$ full-width at half-maximum level. The excitation power was controlled by a gradient neutral density filter and set at 2 mW for all experiments with the exception of the power-dependence measurements. The emission was collected at the right-angle geometry via an $f/2$ collimating lens and subsequently focused by an $f/4$ lens onto the slit of the spectrograph. The (time-resolved) emission detection was performed by a streak camera system equipped with a spectrograph (Hamamatsu C5680) running with the vertical time axis sweep off while recording cw emission spectra.

B. Experimental part: Synthetic Procedures



Scheme S1. Synthesis of IR-806.

Synthesis of IR-806. The functionalization reaction was performed using standard Schlenk-line techniques in dry glassware and under a dry N₂ atmosphere. A mixture of IR-780 iodide (500 mg, 0.75 mmol) and 4-mercaptobenzoic acid (231 mg, 1.50 mmol) in DMF (20 mL) was stirred at room temperature for 17 hours. DMF was removed under vacuum at 40 °C, and the residue was dissolved in CH₂Cl₂ (5 mL). The solution was filtered through a 0.45 µm PTFE syringe filter and then diethyl ether (150 mL) was added slowly to precipitate the product. The precipitate was collected by centrifugation, washed with diethyl ether, and dried under vacuum to afford 506 mg (0.65 mmol, 86%) of gold-colored crystals. ¹H NMR (400 MHz, CDCl₃): δ 8.56 (d, J = 14.1, 2H), 7.94 (d, J = 8.4, 2H), 7.33 (t, J = 7.7, 2H), 7.25 (t, J = 7.6, 4H), 7.17 (t, J = 7.4, 2H), 7.12 (d, J = 8.0, 2H), 6.22 (d, J = 14.1, 2H), 4.11 (t, J = 7.2, 4H), 2.78 (t, J = 5.8, 4H), 2.05 (s, 2H), 1.87 (dd, J = 14.6, 7.3, 4H), 1.41 (s, 12H), 1.02 (t, J = 7.4, 6H). ¹³C NMR (101 MHz, CDCl₃): δ 172.49, 170.63, 148.89, 145.53, 144.47, 142.18, 141.04, 133.94, 131.07, 128.72, 126.70, 125.45, 125.31, 122.18, 111.00, 101.89, 49.20, 46.38, 27.84, 26.77, 20.93, 20.71, 11.68. IR (cm⁻¹): 2961, 2928, 2871, 1716, 1680, 1592, 1539, 1526, 1427, 1395, 1364, 1245, 1229, 1164, 1152, 1084, 1040, 1016, 999, 928, 908, 857, 836, 795, 764, 742, 713, 678. HRMS: calcd for C₄₃H₄₉N₂O₂S [M]⁺: 657.3509; found: 657.3477. Elemental analysis: calcd for C₄₃H₄₉N₂O₂S: C, 65.81; H, 6.29; N, 3.57. Found: C, 65.09; H, 6.23; N, 3.57.

Synthesis of NaYF₄:Yb,Er nanoparticles (NPs). NaYF₄:Yb,Er nanoparticles were synthesized according to the method described in the literature.^[2] The reaction was performed using standard Schlenk-line techniques in dry glassware under a dry N₂ atmosphere. CF₃COONa (544 mg, 4 mmol), Y(CF₃COO)₃·3H₂O (752 mg, 1.56 mmol), Yb(CF₃COO)₃·3H₂O (226 mg, 0.40 mmol), Er(CF₃COO)₃·3H₂O (23 mg, 0.04 mmol), and oleylamine (20 mL) were added to a 100 mL three-neck round bottom flask. With vigorous stirring, the mixture was heated to 100 °C at reduced pressure for 0.5 h to remove water and oxygen, and then heating was continued up to 340 °C in the presence of N₂. After 1 h at 340 °C, heating was stopped. When the reaction

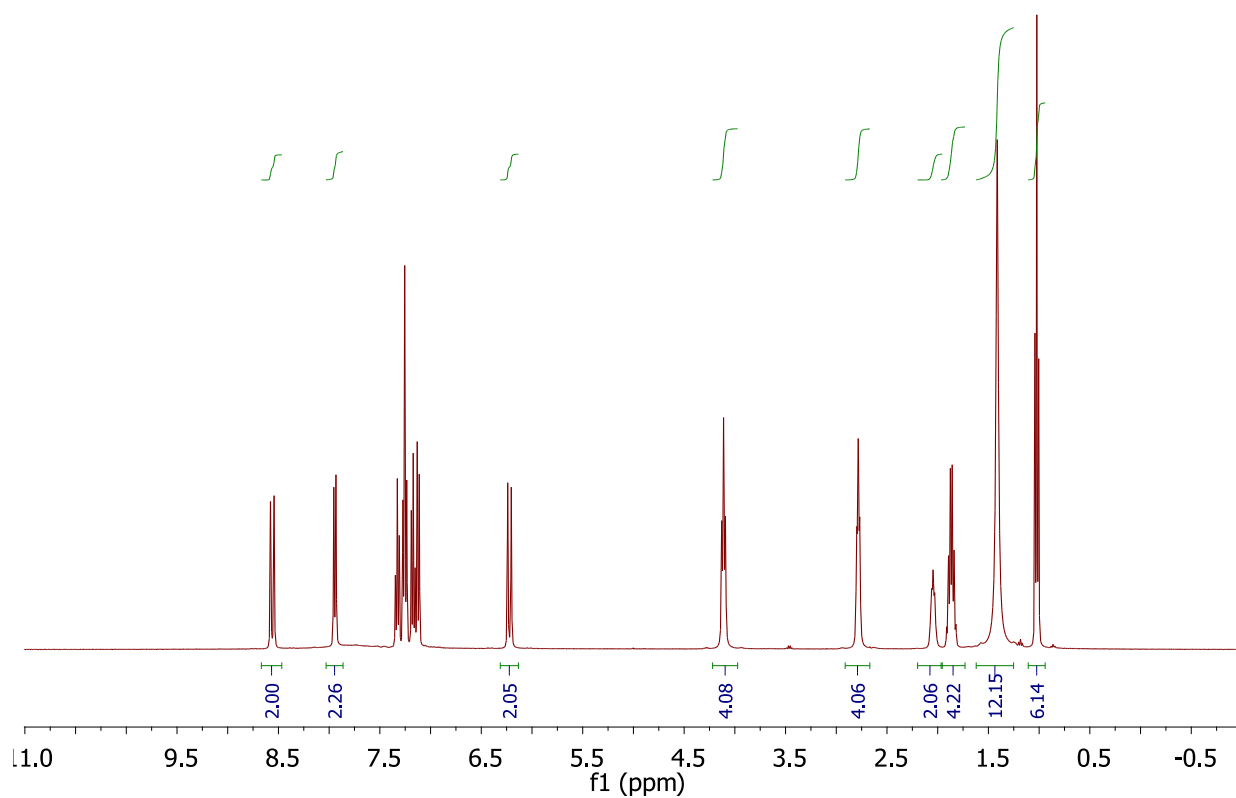
temperature reached 80 °C, ethanol (150 mL) was added. The nanoparticles were isolated by centrifugation. The as-precipitated nanoparticles were washed 3 times with ethanol and then dispersed in 5 mL of chloroform.

Synthesis of NaYF₄ nanoparticles. NaYF₄ nanoparticles were synthesized and purified accordingly, but without the Er and Yb salts added to the reaction.

C. Sample preparation procedures

Sample preparation for IR measurement. A mixture of oleylamine-coated NaYF₄:Yb, Er nanoparticles (50 mg) and IR-806 (1 mg) in CHCl₃ (1 mL) was stirred for 2 h at room temperature under N₂, and then ethanol (20 mL) was added. The IR-806-functionalized NaYF₄:Yb,Er nanoparticles were isolated by centrifugation. The as-precipitated nanoparticles were washed 3 times with ethanol and then dried in a vacuum oven at 40 °C overnight.

Sample preparation for UV-Vis-NIR absorption and fluorescence measurements. All samples were prepared and measured under an atmosphere of N₂. The samples for UV-Vis-NIR absorption and standard fluorescence measurements were prepared by adding different amounts of NaYF₄:Yb,Er nanoparticles to 0.01 mg of IR-806 in CHCl₃ (4 mL). The solutions were stirred for 2 h at room temperature. The samples for upconversion fluorescence measurements were prepared by adding different amounts of IR-806 to 40 mg of NaYF₄:Yb,Er nanoparticles in CHCl₃ (1 mL). The solutions were stirred for 2 h at room temperature and then diluted 50 times for measurement.

D. Spectroscopic and microscopic data:**Fig S1.** ^1H -NMR (400 MHz, CDCl_3) spectrum of IR-806.

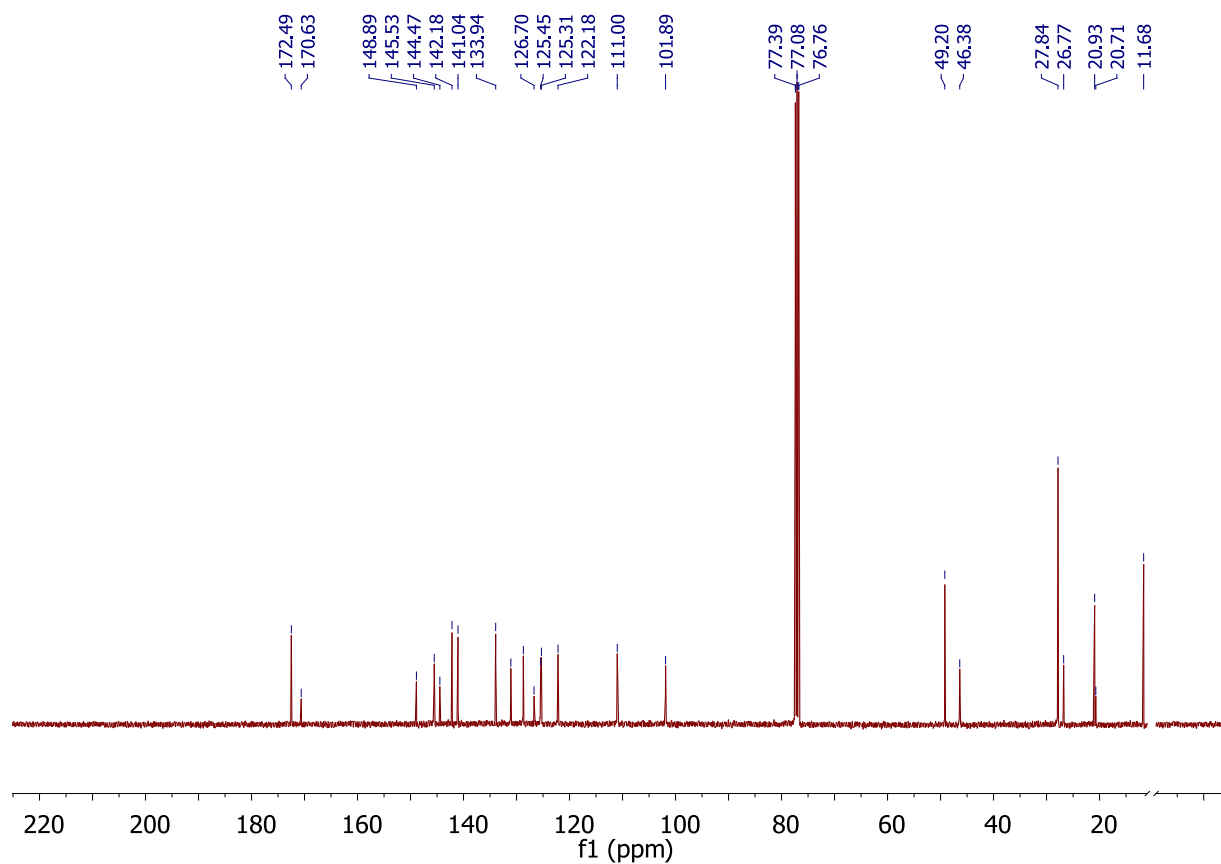


Fig S2. ^{13}C -NMR (101 MHz, CDCl_3) spectrum of IR-806.

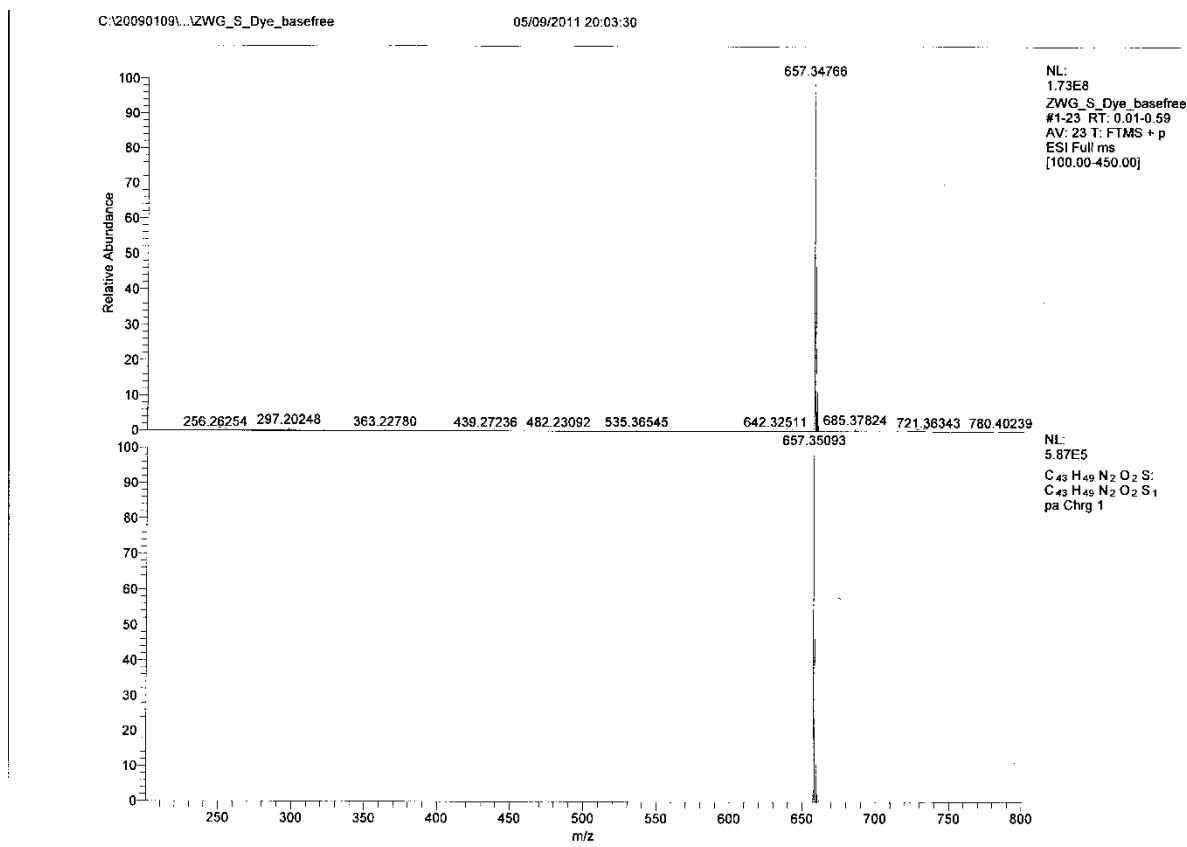


Fig S3. HRMS spectrum of IR-806 (top: experimental result; bottom: calculated).

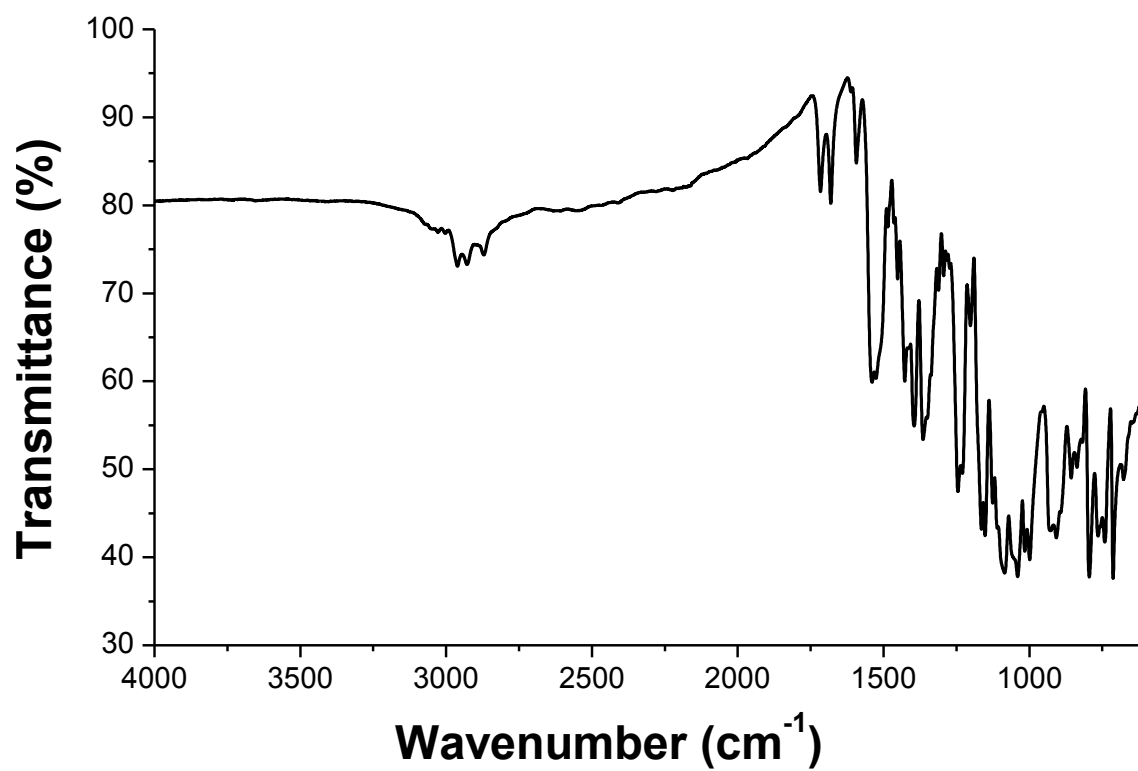


Fig S4. FT-IR (ATR) spectrum of IR-806.

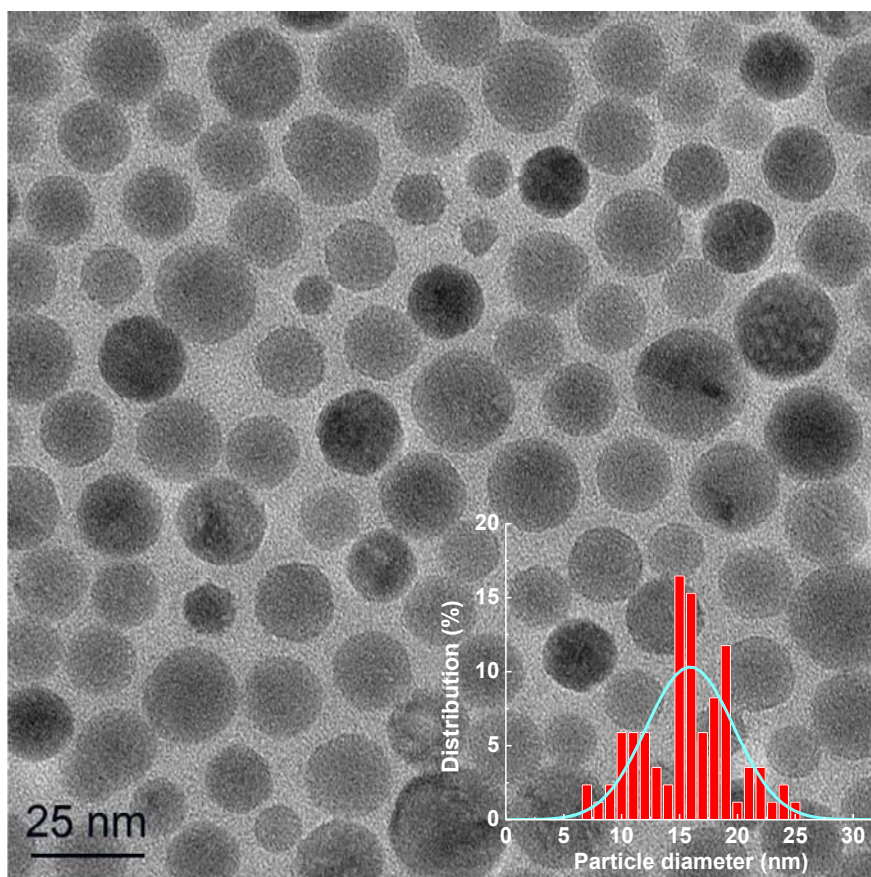


Fig S5. TEM image of NaYF₄:Yb, Er NPs. The inset shows the size distribution calculated from analysis of 85 NPs. The Gaussian fit to the distribution (cyan line) yields the average core diameter of 16 nm with a standard deviation of 7 nm.

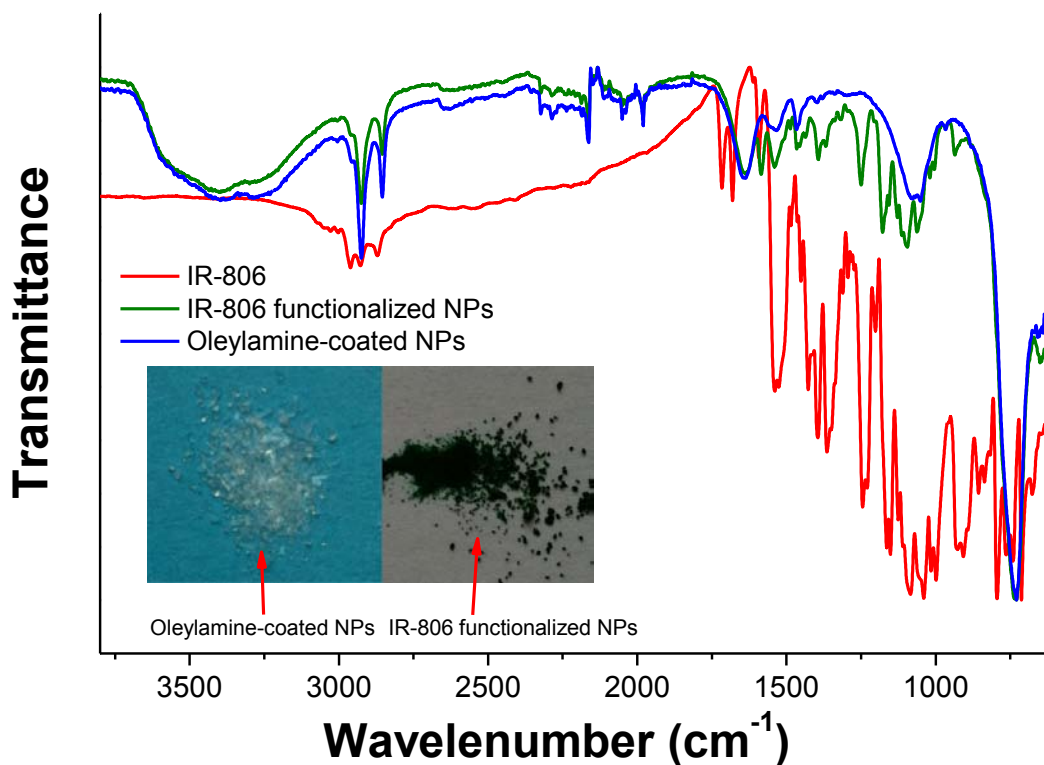


Fig S6. FT-IR (ATR) spectra of IR-806 (red line), oleylamine-coated NPs (blue line), and IR-806-coated NPs (olive line). The IR absorption of the IR-806-coated NPs resembles -for a large part- a superposition of the spectra of the constituents. The changes in the carbonyl region ($\nu = 1650\text{-}1750\text{ cm}^{-1}$) are taken as indicative of bond formation between the IR-806 carboxylic acid group and the inorganic NP core. The inset in the figure shows the color change of the sample from colorless (left image, NPs only) to deep green after coating of the NPs with IR-806 (right image), which clearly shows the binding of IR-806 to the nanoparticles.

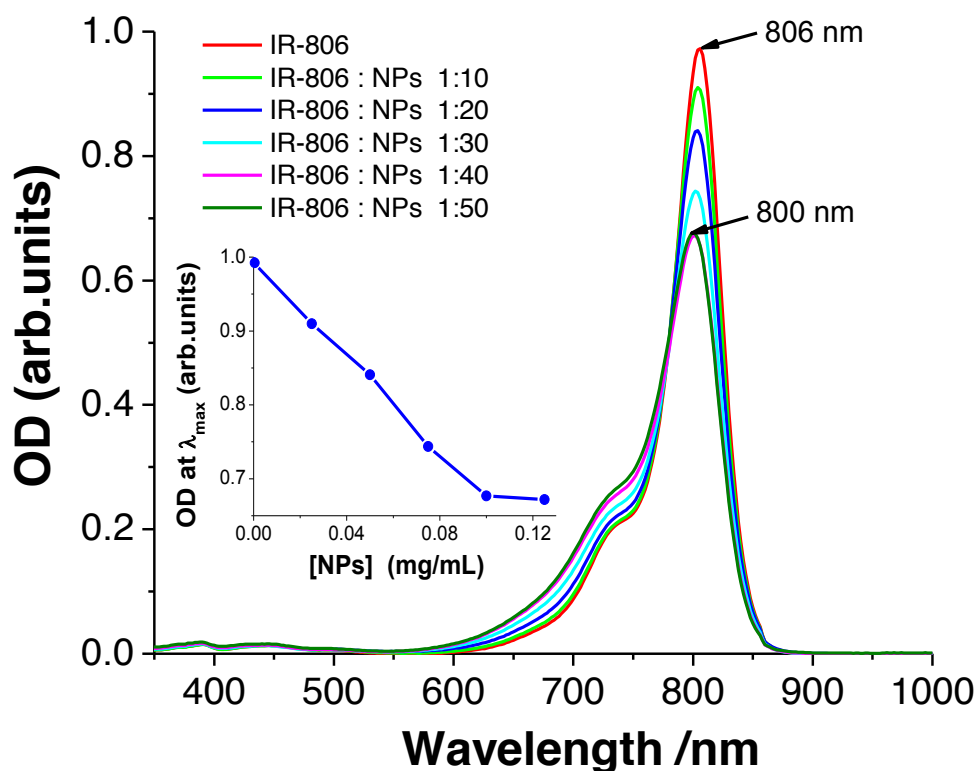


Fig S7a. Change of absorption spectrum of IR-806 (0.0025 mg/mL in CHCl₃) upon increasing concentration of NaYF₄:Yb,Er NPs. The legend shows the weight ratio of IR-806 and NPs. The inset depicts the maximum absorption as a function of the weight content of the NPs, normalized to [NP]=0. Decreased optical density and the blue shift of the maximal-absorption wavelength λ_{max} from 806 nm to 800 nm of IR-806 indicate interactions of IR-806 to the NPs due to their binding.

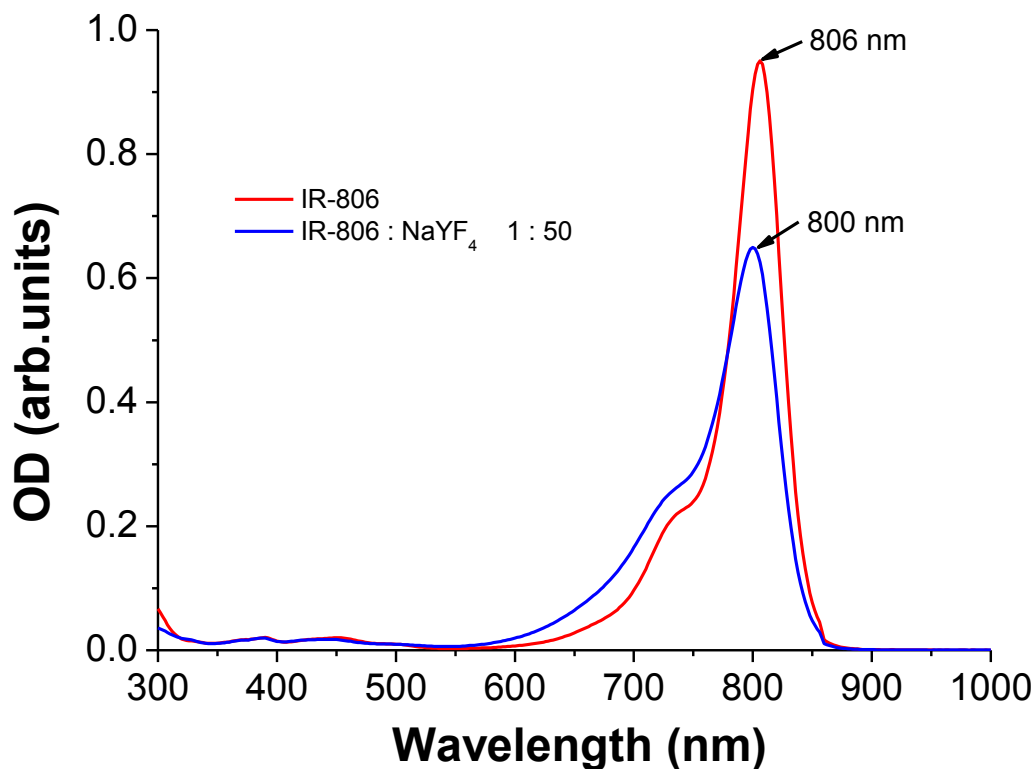


Fig S7b. Change of absorption spectrum of IR-806 (0.0025 mg/mL in CHCl_3) upon addition of *undoped* NaYF_4 NPs (the ‘blank’ NPs). The legend shows the weight ratio of IR-806 and NPs. Upon addition of NaYF_4 NPs, the absorption of IR-806 is blue-shifted from 806 nm to 800 nm, identical to upon adding $\text{NaYF}_4\text{:Yb,Er}$ NPs to IR-806. The OD at λ_{max} decreases by 32% upon addition of NaYF_4 NPs which is consistent with the OD decrease by 30% at λ_{max} upon addition of $\text{NaYF}_4\text{:Yb,Er}$ NPs (see Fig.S7a). Similarly, the OD at 750 nm increased by 17% upon addition of addition of NaYF_4 NPs while the OD at 750 nm increased by 23% upon addition of addition of $\text{NaYF}_4\text{:Yb,Er}$ NPs (see Fig.S7a). This proves that the changes in the absorption spectra are caused by chemisorption of the IR-806 to the NaYF_4 NPs regardless their doping.

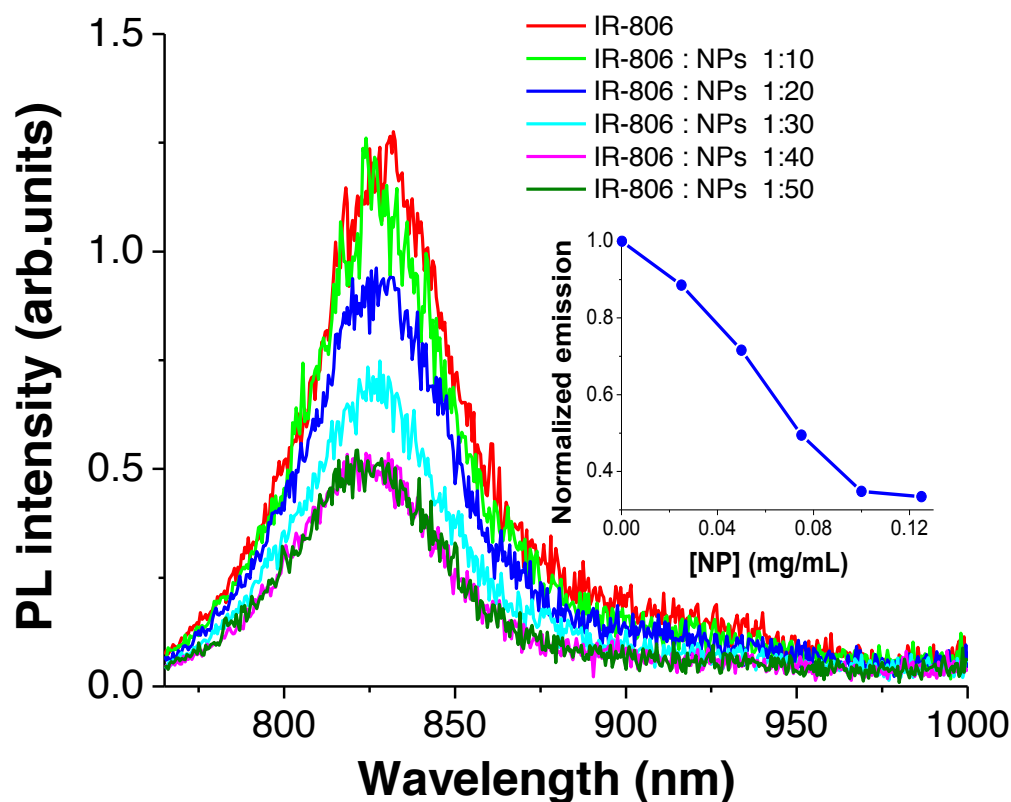


Fig S8a. Change of emission spectrum of IR-806 (0.0025 mg/mL in CHCl₃) upon increasing concentration of NaYF₄:Yb,Er NPs. The excitation wavelength was set at 750 nm where, unlike in peak absorption around 800 nm, the absorption *increases* (by ~30%) with increase of NPs concentration (consult Fig.S7). The legend shows the weight ratio of IR-806 and NaYF₄:Yb,Er NPs. The inset depicts the emission intensity (integrated from 765 to 980 nm) of IR-806 as a function of concentration of NPs, normalized to [NP]=0 and corrected for the increased absorption of IR-806 at 750 nm, see Fig. S7a. The fluorescence intensity is decreased by ~65%.

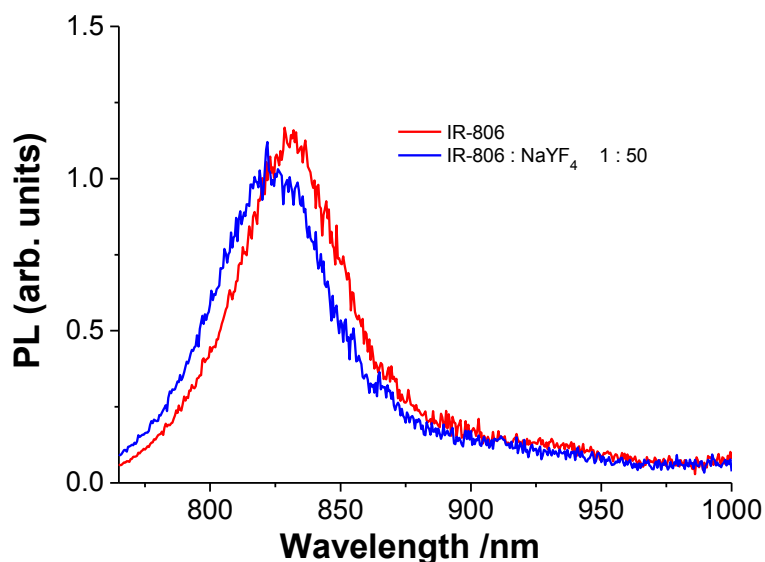


Fig S8b. Change of emission spectrum of IR-806 (0.0025 mg/mL in CHCl_3) upon 50:1 (w/w) addition of *undoped* NaYF_4 NPs (the ‘blank’ NPs). The excitation wavelength was set at 750 nm, as in the experiment depicted in Fig. S8a. The emission intensity of IR-806 decreased by ~11% (corrected for the increased absorption of IR-806 at 750 nm, see Fig. S7b)

The following conclusion is drawn from the experiments depicted in Fig S8a and S8b:

The decrease of emission intensity upon adding $\text{NaYF}_4\text{:Yb,Er}$ NPs to IR-806 was ~65% (Fig S8a), which, together with the mere 10% decrease observed in the blank experiment (Fig.S8b), indicates that ~55% of the energy absorbed by IR-806 is transferred to the Er, Yb photon energy acceptors in the $\text{NaYF}_4\text{:Yb,Er}$ NPs.

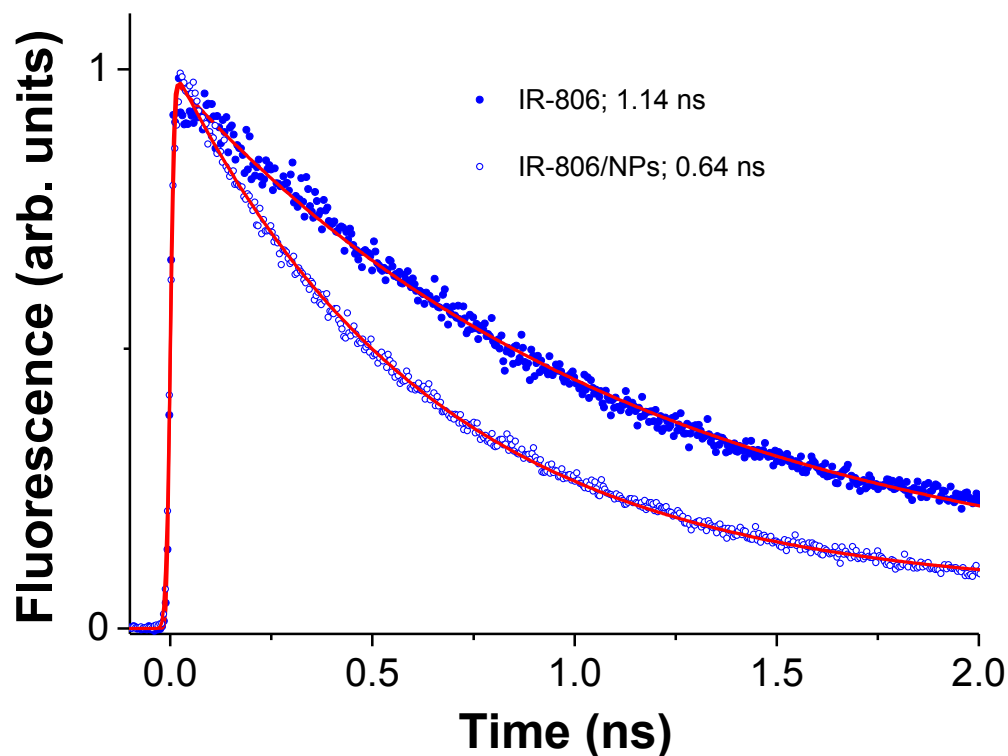


Fig S9. Time-resolved fluorescence of IR-806 (0.0008 mg/mL, blue dots) and IR-806/NaYF₄:Yb,Er NPs (0.0008/12 mg/mL, blue circle) in CHCl₃ excited by a 800 nm, 100 fs pulsed laser (repetition rate of 76 MHz, repetition rate of 3 mW). The red lines are best fits for a monoexponential function. The fluorescence was integrated in the regions of 802–852 nm for IR-806 and 792–842 nm for IR-806/NPs to account for the emission shift due to binding. The ~45% decrease of fluorescence lifetime of IR-806 upon adding NaYF₄:Yb,Er NPs is in reasonable agreement with the ~55% energy transfer from IR-806 to the NPs, as deduced from the experiments depicted in Fig. S8a&b.

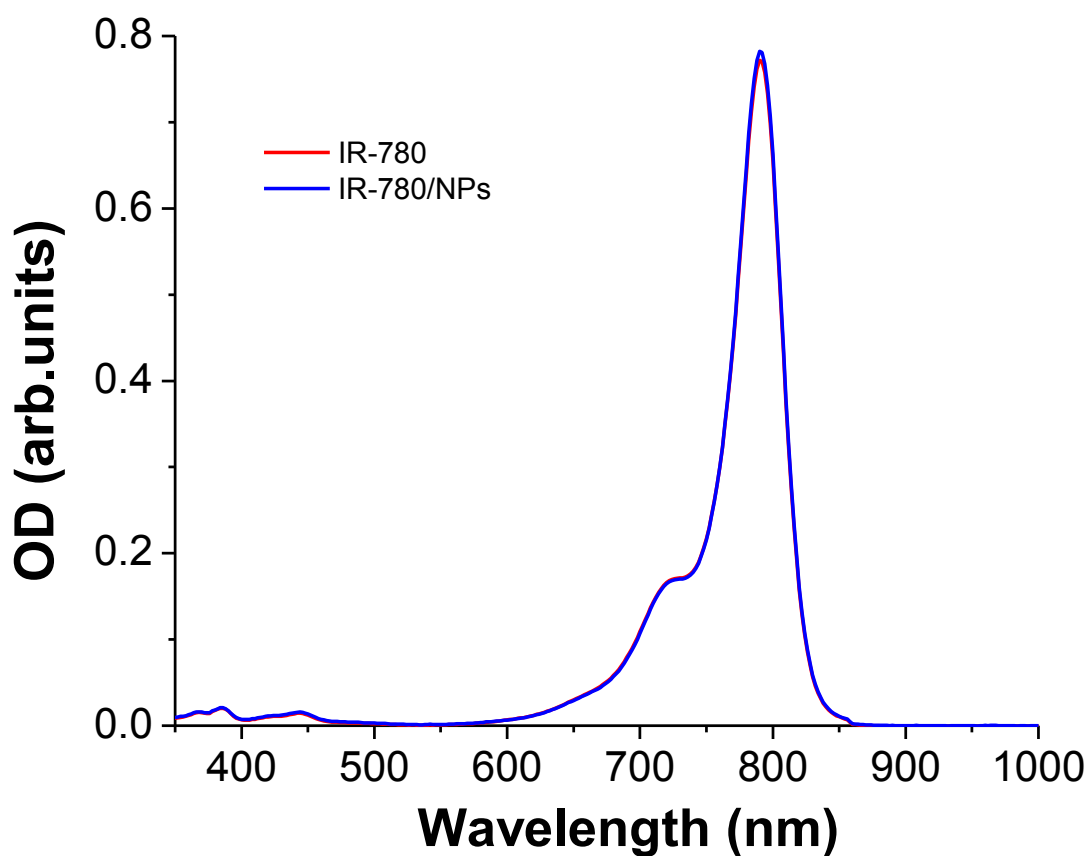


Fig S10. “Blank experiment”: UV-VIS-NIR absorption spectra of the reference dye IR-780 (red line, 0.0025 mg/mL) and IR-780/NPs (blue line, 0.0025/0.125 mg/mL) in CHCl_3 . There is no change of absorption spectrum of IR-780 upon adding NPs which confirms that there is no binding between IR-780 and NPs.

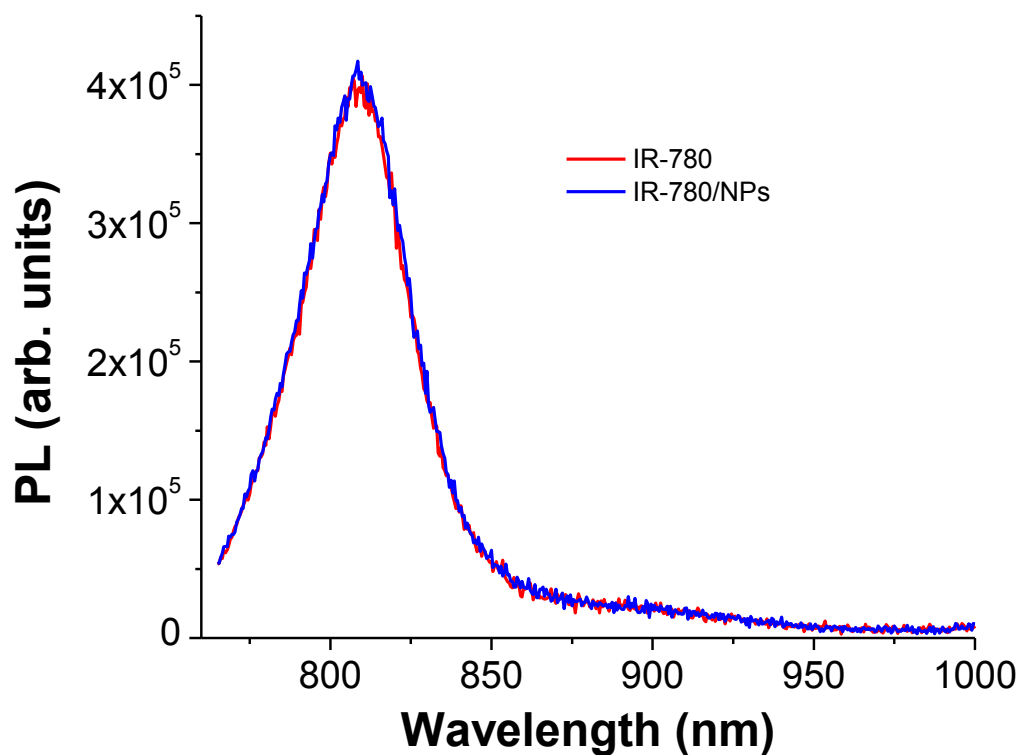


Fig S11. “Blank experiment”: Fluorescence spectra of the reference dye IR-780 (0.0025 mg/mL) and IR-780/ NPs (0.0025/0.125 mg/mL) in CHCl_3 . The excitation wavelength is 750 nm. The emission spectrum of IR-780 does not change after the NPs were added, signifying that chemical modification from IR-780 to IR-806 (Section B above) is required to ensure binding of the antenna molecule to the NPs.

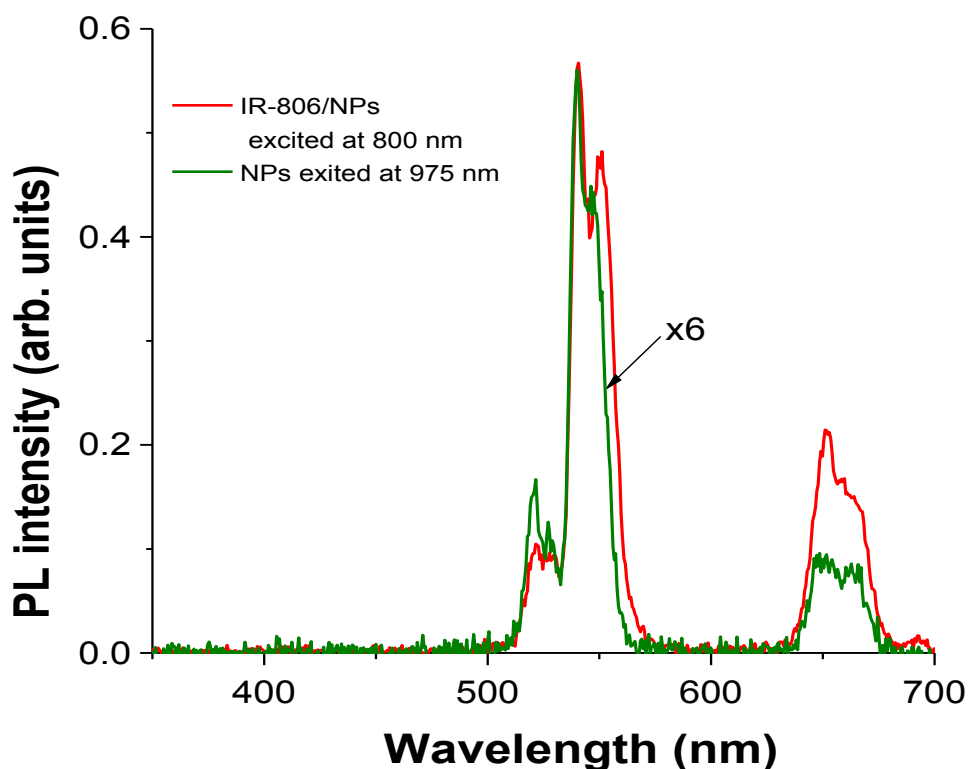


Fig S12. Steady-state emission spectra of IR-806/NPs (red line, 0.80/0.006 mg/mL, excited by a 2 mW, 800 nm cw laser) and NPs (olive line, 4.0 mg/mL, excited by a 50 mW, 975 nm cw laser) in CHCl_3 . Note that the emission intensity from the NPs sample is multiplied by a factor of 6, the NPs sample is excited by a factor of 25 stronger light (which transfers to a factor of 625 in emission considering the two-photon nature of the excitation process), and the concentration of the NPs sample was a factor of 5 higher than in the IR-806/NPs sample to obtain detectable emission. Note that the emission upconversion spectra are similar regardless the NPs or IR-806 excitation at 975 and 800 nm, respectively. This is another evidence for efficient energy transfer from the IR-806 antennas to the NP where the energy is upconverted into the green photons.

E. Estimations on NPs molecular weight, molar antenna:NPs ratio, and average intermolecular distances between antenna molecules on the surface of the NPs

Molecular weight: We begin from the known density of pure NaYF_4 that amounts to $4.21 \text{ g/cm}^3 = 4.21 \cdot 10^{-21} \text{ g/nm}^3$,^[3] which we will also use as the density of our lanthanide doped NPs core. From the averaged NPs core diameter of 16 nm (Fig. S5), the NP volume is calculated (in a spherical approximation) as 2145 nm^3 . From here we arrive at the averaged NP core weight of $2145 \times 4.21 \cdot 10^{-21} = 9.0 \cdot 10^{-18} \text{ g}$, which can be recalculated as molecular weight of $6 \cdot 10^{23} \times 9.0 \cdot 10^{-18} = 5.4 \cdot 10^6 \text{ g/mol}$. Then we add the weight of ~ 5 per nm^2 (i.e. as if densely packed, like in a SAM^[4]) oleylamine molecules (MW 267.5) equally distributed over a 804 nm^2 NP surface area, i.e. $\sim 1 \cdot 10^6 \text{ g/mole}$ for the organic shell. This results in a total value of inorganic core + organic shell average $\text{MW}_{\text{total}} = 6.4 \cdot 10^6 \text{ g/mol}$ for the oleylamine coated NPs.

Molar antenna:NP ratio: Optimum efficiency for the dye-sensitized upconversion was observed at the NPs:IR-806 ratio of 0.8 mg : 0.006 mg, i.e. the weight ratio of 133:1. The molecular weight of IR-806 depends on the counterion: $\text{MW}_{\text{IR-806}} = 657$ without counter anion (656 as internal salt) or 784 as the iodide. We expect that the IR-806 molecules on the NPs may not all have iodide counterions. Therefore, we used the two extreme values for the IR-806 molecular weight in the following estimations. At a weight ratio of 1:133 the IR-806:NP ratio ranges then between 73:1 and 61:1 antennas per particle.

Distances between antenna molecules on the surface of the inorganic core of the NPs: At the optimal $\sim 70:1$ ratio, the core surface coverage is 804 (NP surface area) over 70 (number of antennas at a single NP) = 11 nm^2 per IR-806 molecule, which results in the average center-to-center distance of 3.4 nm. At the “saturation” ratio of $0.0025:0.1 = 1:40$, the IR-806:NP ratio becomes between $\sim 200:1$ and $240:1$ antennas per average size NP, with the averaged center-to-center inter-antenna distance on the surface of the inorganic core the NP of 1.9 nm. Such a short separation most probably results in self-quenching amongst the antenna molecules.

F. Measurement of the Monochromatic Quantum Yield of IR-806/NPs and NPs

To determine the monochromatic quantum yield (mQY) of the IR-806/NPs we chose as a reference sample a DMSO solution of ATTO Rho14 fluorophore with a well-established QY of 80%.⁵ Excitation of the dye solution was performed at a wavelength of 595 nm selected from a home built white-light continuum generator based on a hollow fiber.⁶ The Mira pump laser was run in mode-locked femtosecond mode and the vertical time axis sweep of the streak-camera was switched off (“focus mode”) to record the time integrated emission spectrum. A 20 nm portion of the continuum centered around 595 nm was selected by an interference filter. The sample optical density at 595 nm over 1 mm was measured to be OD=0.035.

We measured the emission intensity of the up-conversion sample, β -NaYF₄:Yb,Er NPs/IR-806 in CHCl₃ at the optimal concentration of 0.80/0.006 mg/mL. Excitation of the IR-806/NPs was performed with the Mira laser in cw mode at a wavelength of 800 nm (OD=0.19 over 1 mm). The green-yellow emission was collected in exactly the same way as the emission from the reference dye sample.

To determine the QY of up-conversion of bare β -NaYF₄:Yb,Er NPs, their solution in CHCl₃ was used at a concentration of 650 mg/mL. Excitation of NPs was performed again in cw laser mode but at a wavelength of 974 nm (OD=0.04 over 1 mm).

Emissions of the reference, IR-806/NPs, and NPs samples were corrected for streak-camera sensitivity and integrated over the 500-700 nm detection range. The sample mQY was calculated according to Eq.1 by Balushev et al.⁷ Note that within this definition, the mQY ranges from 0 to 1 for one-photon and from 0 to 0.5 for two-photon (as the upconversion) processes. The calculated values of the mQY are given in Table 1. The maximum mQY of IR-806/NPs is attained near the saturation regime (see Fig.4 of the main text) and amounts to $0.12^{+0.10}_{-0.05}\%$. This is in a good agreement with the mQY of the NPs sample of $0.3\pm0.1\%$ (obtained at slightly higher excitation intensity) and the dye-NP energy transfer efficiency of $\sim 50\%$.

Table 1. Results of measurements of monochromatic quantum yields

	RHO14	IR-806/NPs			NPs
Excitation power, W	0.003	2	4	8	4
Excitation intensity, W·cm ⁻²	1	200	450	900	650
mQY, %	80	0.08±0.05	0.12 ^{+0.10} _{-0.05}	0.1±0.05	0.3±0.1

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